

A COMPARATIVE STUDY OF THE REACTIONS OF
MESITYL CYCLOPROPYL KETONE AND
MESITYL PROPENYL KETONE

BY
FREDERICK NEIL BAUMGARTNER
A. B., Miami University, 1942

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

Evidence that the cyclopropane ring when adjacent to a carbonyl group acts in a manner analogous to a carbon-carbon double bond was first observed by Bone and Perkin¹ in 1895. The reaction of ethyl cyclopropane-1,1-dicarboxylate and ethyl malonate in the presence of sodium ethoxide produced ethyl butane-1,1,4,4-tetracarboxylate. Various other investigators² have shown that certain cyclopropane carbethoxy derivatives react in a conjugate manner with halogen acids. Ultraviolet spectra of *i*-steroids³ corroborate the conjugation theory. Since little study of cyclopropyl ketones has been reported, the present work was undertaken in an effort to correlate the reactions of these compounds with the reactions of α,β -unsaturated ketones. Mesityl cyclopropyl ketone and mesityl propenyl ketone were selected for study since the carbonyl group in these compounds is unaffected by ordinary carbonyl reagents.

DISCUSSION OF RESULTS

Mesityl cyclopropyl ketone was prepared by three methods. The first two of these syntheses employed the action of the Grignard reagent on cyclopropyl cyanide and cyclopropanecarboxylic acid chloride. The third and best method was the reaction of cyclopropanecarboxylic acid chloride and mesitylene in the presence of anhydrous aluminum chloride. Mesityl propenyl ketone was prepared according to the procedure of Fuson, Christ, and Whitman.⁴ The structure of the cyclopropyl ketone was determined by the manner in which it reacted with various reagents and by infrared analysis.

Mesityl cyclopropyl ketone was found to undergo reaction in a conjugate manner with hydrobromic acid, benzene in the presence of anhydrous aluminum chloride, and mesitylene in the presence of anhydrous aluminum chloride to produce, respectively, γ -bromobutyromesitylene, γ -phenylbutyromesitylene, and γ -mesitylbutyromesitylene. The fact that only the *gamma* derivatives were obtained from the action of benzene and mesitylene excludes the possibility that γ -chlorobutyromesitylene was an intermediate in these reactions. If this compound were an intermediate, both the *beta* and the *gamma* derivatives might be expected, since alkylation of benzene with *n*-propyl chloride is known to produce both *n*-propyl- and isopropylbenzene. Undoubtedly the first step in the reaction is the formation of a polarized aluminum chloride complex which is the active intermediate. Addition of the hydrocarbon to the complex molecule and rupture of the cyclopropane ring occur simultaneously so that no possibility exists for isomerization to take place.

All attempts to condense mesityl cyclopropyl ketone and ethyl malonate were unsuccessful even at elevated temperatures and pressures. Attempted condensation of the ketone with the Grignard reagent also failed. There was some indication that the *halomagnesium* enolate had formed, although the enolate failed to undergo reactions typical of such compounds.

Addition of the Grignard reagent, benzene in the presence of anhydrous aluminum chloride, and ethyl malonate to mesityl propenyl ketone produced the expected *beta* substituted derivatives. The propenyl ketone also was found to undergo condensation in the aldol manner with *p*-chlorobenzaldehyde to produce *p*-chlorocinnamalacetomesitylene. Mesityl cyclopropyl ketone did not undergo condensations of the aldol type.

Thus mesityl cyclopropyl ketone apparently reacts in a manner analogous to α,β -unsaturated ketones only in acidic

media. Conjugate addition has not been observed with basic catalysts.

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VITA

The author was born in Bluffton, Ohio, on June 4, 1920. He attended the public schools of that town and was graduated from Bluffton-Richland High School in May, 1938. In the fall of the same year, he entered Miami University at Oxford, Ohio, and received the degree of Bachelor of Arts in June, 1942. The same month he entered the Graduate College of the University of Illinois. He held a teaching assistantship from September, 1942, until November, 1942, at which time he was called into the armed services. He served in the Army Air Forces from November, 1942, until January, 1946, both in the United States and in the South Pacific. He reentered the Graduate College of the University of Illinois in March, 1946. He held a teaching assistantship from March, 1946, until July, 1947, and a University of Illinois Fellowship during the academic year of 1947-1948.



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